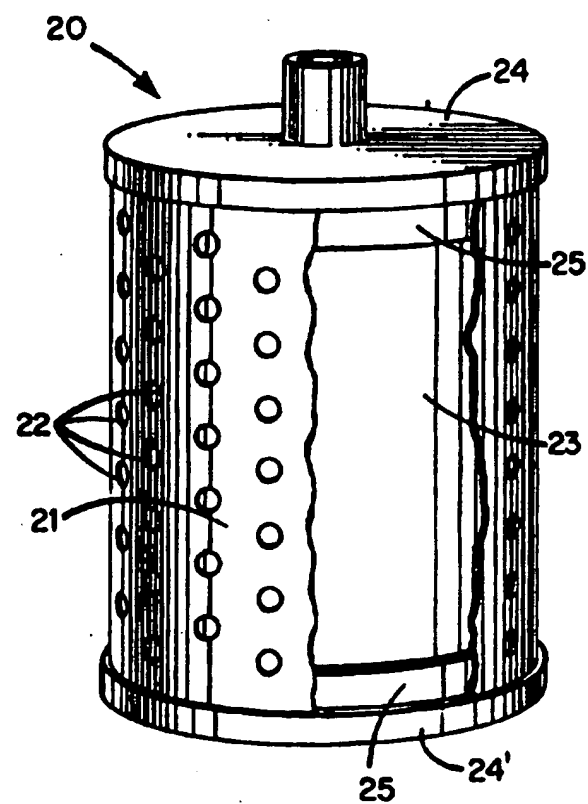


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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US95/01175 (22) International Filing Date: 26 January 1995 (26.01.95) (30) Priority Data: 08/338,998 14 November 1994 (14.11.94) US (71) Applicant: W.L. GORE & ASSOCIATES, INC. [US/US]; 551 Paper Mill Road, P.O. Box 9206, Newark, DE 19714 (US). (72) Inventors: KLEMENCIC, James, F.; 20 Oak View Drive, Newark, DE 19702 (US). TILLEY, Mary, W.; 339 Great Oak Drive, Middletown, DE 19709 (US). (74) Agents: SAMUELS, Gary, A. et al.; W.L. Gore & Associates, Inc., 551 Paper Mill Road, P.O. Box 9206, Newark, DE 19714 (US).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: HYDROPHILIZED FILTER CARTRIDGE AND PROCESS FOR MAKING SAME (57) Abstract <p>To make hydrophobic membranes useful in aqueous filtration applications, the membranes are hydrophilized. But, in assembling filter cartridges, the hydrophilizing agents, effectiveness can easily be impaired if heat is applied in making the cartridge. This affects the integrity testing of the assembled cartridge. To overcome the apparent failure of a filter cartridge (20) in integrity testing in water, the edges of the membrane are rendered impervious to air flow. The strip of filter membrane (23) is treated along each edge by laminating a nonporous strip (25) to the edge, or by densifying it. The membrane (23) is then treated with a hydrophilizing polymer. The treated membrane can then be shaped into the form of a cylinder, usually pleated, and then is thermally bonded at its ends to a filter cartridge support structure. Because the bonding occurs in the area impervious to air flow, the hydrophilic treatment of the other areas is not destroyed. The filter media is now able to pass the integrity test described above.</p> 		

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TITLE OF THE INVENTION**HYDROPHILIZED FILTER CARTRIDGE AND
PROCESS FOR MAKING SAME**

5

FIELD OF THE INVENTION

This invention relates to a process for making integrity testable hydrophilic filter cartridges and to filter cartridges made by the process.

10

BACKGROUND OF THE INVENTION

Filter media which are made of porous membranes are commonly made of a fluoropolymer, which is a hydrophobic material. One such filter medium is made of stretched porous polytetrafluoroethylene. These filters are strong and chemically inert, making them desirable for use as filters. However, being hydrophobic, they are not as useful in aqueous filtration systems as desired. But because of their strength and inertness, it has been a goal to render these hydrophobic filter media hydrophilic so that they may be used in aqueous systems.

20

By "hydrophobic" is meant that a material referred to is resistant to wetting with water. By "hydrophilic" is meant that a material referred to is water-wettable. As applied to a description of filter media, the terms indicate whether the media is resistant to penetration by water or readily passes water through it.

25

Ordinarily, the porous membrane used as the filter medium is treated with a hydrophilizing polymer and then the filter cartridge is assembled. It is common to use thermal sealing processes to bond the filter membrane to the cartridge housing. Typical materials of construction for these housings include polytetrafluoroethylene, or tetrafluoroethylene copolymers or other fluoropolymers or polyolefins. Thus, bonding temperatures may range from 160°C to 400°C.

30

In the regions next to and including these thermally bonded areas, the hydrophilizing polymer's effectiveness is significantly lessened by the heat, and the hydrophilic property of these areas is lost. While this loss of hydrophilicity does not appreciably affect total aqueous liquid flow through the filter membrane, it does render standard aqueous integrity tests ineffective.

35

Integrity testing is performed in order to make certain that there are no pinholes in the membrane or defects at the bonding sites. Integrity testing for hydrophilic porous filter media is preferably carried out by completely wetting the pore structure of the membrane with water and applying air pressure to the cartridge. Air flow through the cartridge is then measured. If the measured flow is negligible, the cartridge is considered integral. If excessive air flow is detected, the cartridge fails the test. Ordinarily this excessive air flow is attributed to a physical defect in the cartridge.

However, in the case where treated membranes have lost their imparted hydrophilicity due to the heat associated with cartridge manufacture, the hydrophobic regions near the bonding sites will not be wetted by water. Therefore, these unwetted regions will allow air flow on the order of that which would typically be seen in a defective hydrophilic cartridge. Thus, an integral hydrophilic cartridge with no defects but some hydrophobic regions cannot be distinguished from a defective hydrophilic cartridge.

Such a hydrophilic device can be integrity tested with a low surface tension fluid such as alcohol that will wet both hydrophilic and hydrophobic regions. This is undesirable because it requires introducing a contaminant, namely the wetting fluid which must then be flushed out.

SUMMARY OF THE INVENTION

To overcome this apparent failure of such cartridges in integrity testing, a strip of porous hydrophobic membrane is initially treated along each edge to render the area along each edge impervious to air flow through it. This can be accomplished either by laminating a nonporous strip to the edges to prevent air flow through that area of the membrane or by densifying the edges in order to compress the material to the extent that the pores are eliminated. The material is then treated with a hydrophilizing polymer. The treated construction can then be shaped into any appropriate configuration for the filter cartridge and thermally bonded along the nonporous areas. Even though the thermal bonding has rendered the hydrophilic polymer ineffective at the bonding sites, the membrane does not allow air flow in those areas, so the filter cartridge is now able to pass the integrity test described above.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts the procedure by which lamination of the filter membrane to the nonporous strips on opposite edges occurs.

5 Figure 2a depicts the product of the lamination from the top and Figure 2b depicts a side view of the product.

Figure 3 is a cutaway view of a filter cartridge with the filter membrane inside.

10 Figure 4 depicts a side view of a membrane in which the opposing edges have been densified as denoted by the crosshatching.

DETAILED DESCRIPTION OF THE INVENTION

15 The membranes that can be treated by this invention can be any microporous or porous material that is utilized for filtration purposes. These have continuous pores from one side to the other. Thus, by "porous" and "microporous" is meant that the membrane has continuous passageways from one side to the other. As long as continuous pores are present in the membranes, the method for forming such pores is not restricted to a particular
20 method. For example, stretching (i.e., expanding), bubbling, extraction, and the like may be used. The membranes are usually hydrophobic and are usually composed of fluoropolymers such as polytetrafluoroethylene, or polyvinylidene fluoride or copolymers of tetrafluoroethylene. They can also be composed of polyolefins such as polypropylene and polyethylene.

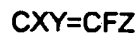
25 Preferably the starting membrane is a hydrophobic fluoropolymer. Stretched polytetrafluoroethylene is an especially preferred membrane. It can have a porosity ranging usually from 15% to 95%, preferably from 50% - 95%.

30 The hydrophilizing medium can be a solution of any hydrophilic polymer which when deposited on the surface of the hydrophobic membrane, raises the surface free energy of the membrane so that it becomes more wettable by water. The requirements that must be met by this system are that the solution concentration be appropriate to the pore structure of the membrane being treated and that this membrane be readily wetted by the solvent. If the
35 membrane is not directly wetted by the solvent, appropriate pre-wetting of the membrane should be accomplished so that the membrane will readily receive the hydrophilizing solution.

One type of hydrophilizing polymer that can be used is a copolymer of a fluorine containing ethylenically unsaturated monomer and a non-fluorinated

vinyl monomer containing a hydrophilic group. Other polymers can be used including polyvinyl alcohol, and the like.

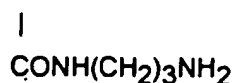
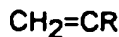
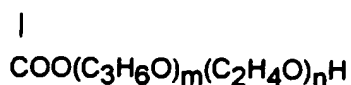
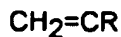
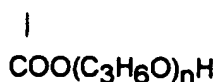
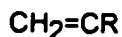
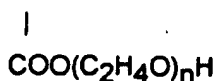
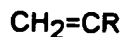
Preferably the fluorine-containing, ethylenically unsaturated monomer will be a vinyl monomer such as, for example, tetrafluoroethylene, vinyl fluoride, vinylidene fluoride, monochlorotrifluoroethylene, dichlorodifluoroethylene, hexafluoropropylene, and the like. More broadly, the fluorine-containing monomer can be described as



wherein Z can be fluorine or hydrogen and X and Y can each be selected from hydrogen, fluorine, chlorine and CF_3 .

The monomers that contain hydrophilic groups include those that have hydroxyl groups, carboxyl groups, sulfate groups, phosphoric acid groups, amide groups that may be N-substituted, and amino groups that may be N-substituted, or the like. Monomers in which an alkylene oxide such as ethylene oxide or propylene oxide has been subjected to an additional reaction with the active hydrogen in these groups are also useful. Those that yield copolymers containing hydrophilic groups by performing first copolymerization and then saponification, as for example, polymers containing vinyl acetate units, are also useful.

Specific examples of these monomers include vinyl acetate, acrylic acid, methacrylic acid and other such unsaturated carboxylic acids, as well as alkylene oxide adducts of acrylic acid or methacrylic acid, such as those shown below:



In the above formulae, R is hydrogen or a methyl group and n and m are integers greater than or equal to one and preferably one to twenty.

5 The fluorine content of the fluorine-containing hydrophilic polymer used in the present invention may range usually from 2% to 60%, preferably from 10% to 60%, and most preferably 20%-60% on a weight basis. On the one hand, if the fluorine content of the fluorine-containing hydrophilic polymer becomes too high, the hydrophilic properties of the polymer may be lessened, though the heat resistance may increase. On the other hand, if the fluorine
10 content becomes too low, adhesion of the polymer to the porous fluoropolymer membrane may be reduced and the heat resistance may be decreased.

A preferred copolymer for treating fluoropolymer membranes is a copolymer of vinyl alcohol and a fluorine containing monomer. It can be obtained by preparing a copolymer of vinyl acetate with a fluorine containing
15 monomer and then saponifying the acetate functions to hydroxy functions. The saponification can be carried out to the extent needed to provide the copolymer with hydrophilic properties. An example of such a polymer is a copolymer of tetrafluoroethylene and vinyl acetate. The acetate groups are then converted to -OH groups. These copolymers are more fully described in
20 U.S. Patent 5,130,024 to Fujimoto, et al., incorporated herein by reference.

A typical tetrafluoroethylene/vinyl alcohol (TFE/VOH) copolymer treatment solution is a 1% (by weight) solution of TFE/VOH where the solvent is methanol/ethanol in a 4:1 ratio. The composition by weight of TFE is 25% and VOH is 75%.

25 The filter cartridge can be any type of cartridge, and is not limited to any specific configuration. A representative cartridge is described in PCT WO93/09862. This publication describes a cylindrical cartridge having a cylindrically pleated filter medium. Other types of cartridges that can be used include ones using stacked disk filter media, hollow fiber filter media, and the
30 like. A typical filter cartridge 20 is shown in Figure 3 which comprises a support structure made of cage 21, end caps 24 and 24', an interior core (not shown), and a filter media 23 shown in the cutaway section of cage 21. Cage 21 has perforations 22 to facilitate passage of aqueous liquid. The nonporous thermoplastic strips are shown as 25 located at each end of the membrane
35 under the potting.

Referring to Figures 1, 2a, and 2b, to make the membrane with the nonporous strips laminated to it at each end, a strip of membrane 11, preferably stretched porous PTFE obtained from W. L. Gore & Associates,

Inc., is laminated along the edges of opposing sides with a thin strip of a nonporous polymer 12. The strip is preferably a thermoplastic such as a polyolefin, polyester, polyamide, or a fluoropolymer such as Teflon PFA, Teflon FEP, PVDF, and the like, by applying heat and/or pressure. A
5 convenient method is to feed the strips and membrane between the nips of heated roll 13 and roll 14. A preferred strip is made of polypropylene.

The membrane is then hydrophilized by treating the laminate with the hydrophilizing polymer. The hydrophilizing solution can be metered onto the porous filter membrane, thereby coating the pores of the membrane with the
10 hydrophilizing polymer, as the membrane moves along a belt.

The treated membrane is then dried, preferably in an oven.

Alternatively, the opposing sides of the membrane can simply be densified along the edges, by subjecting the edges to pressure sufficient to densify the edges as shown at 15 in membrane 11 of Figure 4. Densification
15 can be achieved by the use of opposing hard nip rolls or the like.

EXAMPLE

A sheet of stretched, porous polytetrafluoroethylene, about 18 inches by
20 50 feet, was laminated along two edges with strips of polypropylene about two inches by 50 feet by passing the membrane with the strips on it through the nips of heated rolls, heated at 220°C and at a nip pressure of 50 psi.

A solution of a hydrophilizing copolymer was prepared by dissolving TFE/VOH copolymer in a solvent mix of 4:1 methanol/ethanol to obtain a 1%
25 by weight solution of the copolymer. The copolymer was 25 weight % tetrafluoroethylene and 75 weight % vinyl alcohol.

To simulate typical cartridge manufacturing conditions, the above membrane, with the nonporous strips, was exposed to molten polypropylene beads at about 200°C.

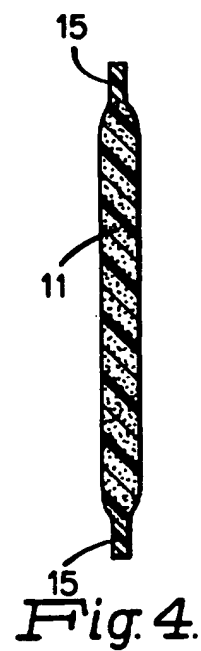
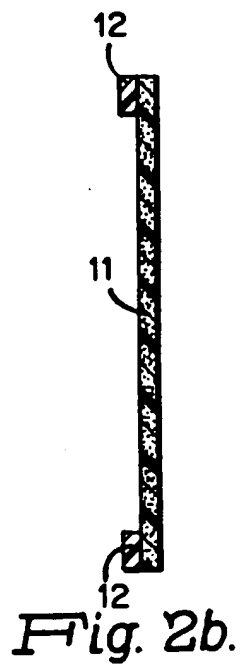
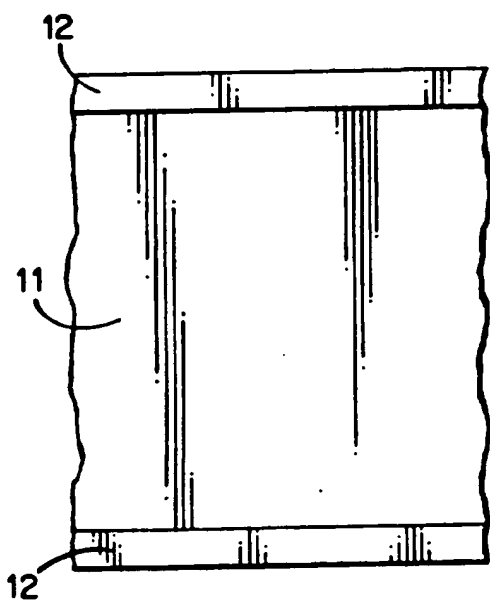
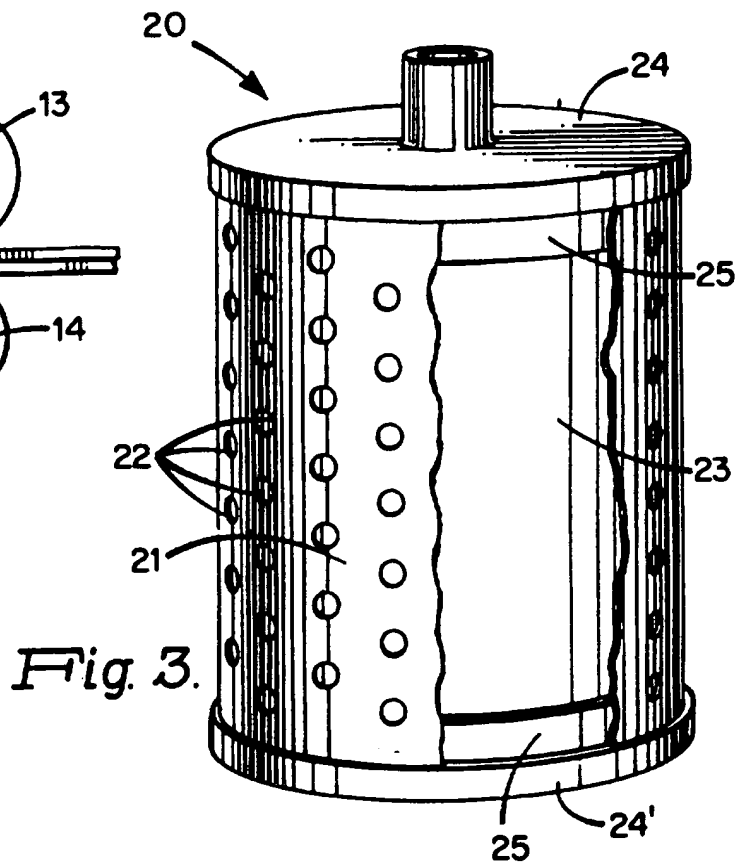
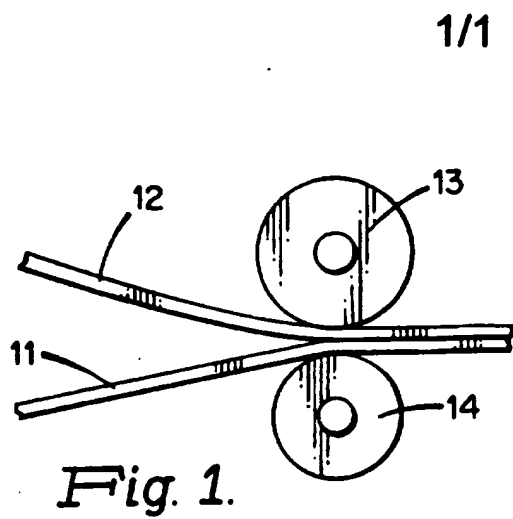
30 Integrity testing was performed by immersing the construction in water, applying air pressure, and measuring the flow of air through the treated membrane.

Air flow through the construction was negligible. Such a construction when manufactured into a cartridge, would pass an integrity test in water.

35 In a similar fashion, cartridges in which the filter medium is made of polyvinylidene fluoride or a polyolefin such as polypropylene can be treated.

WE CLAIM:

1. A filter cartridge comprising:
 - (a) a support structure for a filter medium, and
 - 5 (b) a filter medium affixed to said structure, said filter medium consisting essentially of a hydrophilized porous membrane having the area where the membrane is thermally bonded to the structure rendered impervious to flow of air.
2. A filter cartridge comprising:
 - 10 (a) a support structure for a filter medium, and
 - (b) a filter medium affixed to said structure, said filter medium consisting essentially of a hydrophilized porous membrane having a strip of nonporous thermoplastic polymer covering the membrane in the area where the membrane is thermally bonded to the
 - 15 structure.
3. A filter cartridge comprising:
 - (a) a support structure for a filter medium, and
 - (b) a filter medium affixed to said structure, said filter medium consisting essentially of a hydrophilized porous membrane having
 - 20 the area where the membrane is thermally bonded to the structure, rendered impervious to flow of air, by densifying said areas.
4. The filter cartridge of Claim 1, 2 or 3 wherein the cartridge is in the form of a cylinder and the filter medium is a hydrophilized membrane of stretched porous polytetrafluoroethylene shaped in the form of a pleated
- 25 cylinder, said membrane having a strip of polypropylene around each end in the area where the cylindrical membrane is affixed to the cartridge support structure.
5. A process for making a filter cartridge which comprises:
 - 30 (a) laminating a porous membrane with a narrow strip of nonporous, thermoplastic polymer at two edges of said membrane;
 - (b) treating the laminate with a hydrophilizing polymer;
 - (c) attaching the laminate to a filter cartridge by thermally bonding the laminate to the structure in the region of the strips of nonporous, thermoplastic polymer.
- 35 6. The process of Claim 5 wherein the porous membrane is stretched polytetrafluoroethylene.
7. The process of Claim 6 wherein the thermoplastic polymer is polypropylene.



INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 95/01175

A. CLASSIFICATION OF SUBJECT MATTER

B 01 D 27/00, B 01 D 39/16, B 01 D 46/54, B 01 D 69/10,
B 01 D 71/26, B 01 D 71/36

According to International Patent Classification (IPC) or to both national classification and IPC 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B 01 D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO, A, 94/22 553 (W.L. GORE & ASSOCIATES) 13 October 1994 (13.10.94), claims.	1, 4
A	WO, A, 93/09 862 (MEMTEC AMERICA CORPORATION) 27 May 1993 (27.05.93), claims.	1, 4
A	WO, A, 93/23 153 (COSTAR CORPORATION) 25 November 1993 (25.11.93), claims.	1
A	EP, A, 0 456 939 (JAPAN GORE-TEX) 21. November 1991 (21.11.91), claims.	1

☐ Further documents are listed in the continuation of box C.☐ Patent family members are listed in annex.

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Date of the actual completion of the international search
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Date of mailing of the international search report

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ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/US 95/01175 SAE 104827

In diesem Anhang sind die Mitglieder
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nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
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This Annex lists the patent family
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Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
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WG A1 9323153	25-11-93	EP A1 641249 US A 5376273	08-03-93 27-12-94
EP A1 456939	21-11-91	DE C0 69017197 EP B1 456939 US A 5130024 JP A2 4139237 JP A2 5301033 JP A2 5301991	30-03-93 22-02-93 14-07-93 13-05-93 16-11-93 16-11-93

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